

**FLUID-EVAPORATION RECORDS PRESERVED IN MERIDIANI ROCKS.** M. N. Rao<sup>1</sup>, L. E. Nyquist<sup>2</sup> and S. R. Sutton<sup>3</sup>, <sup>1</sup>ESCG-Jacobs, Johnson Space Center, Houston, TX. 77058; <sup>2</sup>ARES, Johnson Space Center, Houston, TX. 77058; <sup>3</sup>Department of Geological Sciences and CARS, University of Chicago, Chicago, IL. 60637.

**Introduction:** We have shown earlier that the high  $\text{SO}_3/\text{Cl}$  ratios found in secondary mineral assemblages in shergottite GRIM glasses (Gas-Rich Impact-Melt) likely resulted from interactions of regolith materials with sulfate-rich (and Cl-poor) solutions [1,2]. The low  $\text{SO}_3/\text{Cl}$  ratios determined in secondary salts in nakhlite fracture-fillings presumably formed by rock interactions with chloride-rich (and  $\text{SO}_4$ -poor) solutions near Mars surface [1,2]. The  $\text{SO}_3$  and Cl abundances determined by APXS in abraded rocks (RAT) from Endurance, Fram and Eagle craters indicate that these salt assemblages likely formed by evaporative concentration of brine fluids at Meridiani [3,4]. The  $\text{SO}_3/\text{Cl}$  ratios in the abraded rocks are examined here, instead of their absolute abundances, because the abundance ratios might provide better guide-lines for tracking the evolution of evaporating fluids at Meridiani. The  $\text{SO}_3/\text{Cl}$  ratios in these samples, in turn, might provide clues for the mobile element ratios of the altering fluids that infiltrated into the Meridiani rocks.

The absolute  $\text{SO}_3$  and Cl abundances in these rock samples depend on the modal abundances of the mobile element-bearing phases such as sulfate and chloride and mobile element poor phases such as silica and hematite in a given rock volume analysed by APXS. Differential occurrence/mixing of accessory mineral phases (phase-mixing) in one sample relative to another in the rock could lead sometimes to random variations in elemental concentrations of the salts. Furthermore, unknown geometry effects during sample measurements by APXS could lead to apparent variations in the real salt content of a given sample.

Here, we study the inter-relationships between the major anions ( $\text{SO}_4$ , Cl and Br) and cations (FeO, CaO and MgO), using elemental abundances determined by APXS, in abraded rocks at Endurance, Fram and Eagle craters with a view to characterize the composition and behavior of the fluids that infiltrated into these rocks.

**Experimental:** Mobile element abundances in salt assemblages in abraded Meridiani rocks (RAT) as determined by APXS are taken from [3-6].

**Results and Discussion: Sulfate-Chloride system**  $\text{SO}_3$  and Cl abundances determined on abraded Meridiani rocks [3-6] are plotted as  $\text{SO}_3/\text{Cl}$  versus Cl in Fig.1.

The concentrations of conservative ions in the evaporating solutions increase in such a way that their ratios remain constant as water is removed from the system. Further, their relative abundances vary along a

straight line prior to the onset of insoluble salt precipitation. That is, in the case of conservative elements such as S, Cl and Br, when we plot Cl along the ordinate and the  $\text{SO}_3/\text{Cl}$  ratios along the abscissa, the data points might yield a smooth curve (slope convex downward) (Fig.1), suggesting a possible hyperbolic distribution [7,8]. Data points for 20 rocks and outcrops (RAT) from Eagle, Fram and Endurance craters at Meridiani are plotted in Fig.1. The data points are fitted by a hyperbolic function of the type,  $(\text{SO}_3/\text{Cl})_m = p / \text{Cl} + q$ , using the Sigma Plot TM Software. Here, the x-variable is  $(\text{Cl})_m$  and the y-variable is  $(\text{SO}_3/\text{Cl})_m$ . The property of this relationship is that it allows a transformation into a straight line by plotting the x-coordinate as inverse of Cl-abundance, i.e.  $1/(\text{Cl})_m$ , shown in Fig.2. The goodness of fit for the plotted data points in Fig. 2 provides a test for the validity of the assumption that  $\text{SO}_3$  and Cl behave conservatively in acidic solutions on Mars. The  $\text{SO}_3/\text{Cl}$  and Cl data plotted in Fig.2 fit to a straight line ( $r^2 = 0.97$ ). This data-fit indicates that the sequence of evaporative concentration in solutions bearing sulfates and chlorides at Endurance, Fram and Eagle had taken place in an orderly progression (not random precipitation of salts with these anions).

**Chloride-Bromide system.** Cl and Br behave as conservative tracers in Martian fluids [1,2]. This inference is based on the results obtained by comparing Cl and Br abundances in salt assemblages in nakhlites with those obtained from abraded rocks (RAT) at Meridiani [1-4]. Martian meteorites revealed that the salt assemblages in Nakhla yield high Br (~250 ppm) and low Cl/Br ratios (~10-15) suggesting that salt formation took place from relatively concentrated fluids belonging to advanced stages of evaporation on Mars. On the other hand, Lafayette iddingsite [1, 2] yielded low Br (~11 ppm) and high Cl/Br ratios (~250-300) indicating salt formation from relatively dilute solutions related to early evaporation stages. Furthermore, the halogen ratios in these Martian meteorites are consistent with the petrographic evidence recording the sequential deposition of secondary mineral phases, i.e. carbonate-sulfate-halite, preserved in nakhlite veins during evaporative concentration of brine fluids on Mars [1,2].

As in the case of Figs. 1 and 2, we plot the Cl/Br vs Br (figure not shown) and Cl/Br vs  $1/\text{Br}$  (Fig.3) for the same set of rocks (only above the Whatanga contact) at Meridiani. The nomenclature used for these rocks in Figs. 2 and 3 are same as in the case of [3,4].

The data points of  $\text{Cl}/\text{Br}$  plotted against  $\text{Br}$  (figure not shown) for Meridiani abraded rocks above the Wha-tanga contact yield a hyperbolic distribution which is transformed into a straight line ( $r^2=0.94$ ) on plotting  $\text{Cl}/\text{Br}$  versus  $1/\text{Br}$  in Fig.3. This result reaffirms that the chloride and bromide in the fluids that gave rise to these evaporite salts in Meridiani rocks behaved conservatively. This behavior is similar to that of the sulfate-chloride system in these rocks. Such closely-coupled chemical behavior between these three anions could perhaps be achieved only in fluids that are fairly acidic in character.

**FeO/CaO/MgO –  $\text{SO}_3/\text{Cl}$  system:** The abundance profiles of CaO/MgO and FeO/MgO ratios with respect to  $\text{SO}_3/\text{Cl}$  in the abraded Meridiani rocks (Fig.4) are quite similar to one another suggesting that divalent Fe likely precipitated as sulfate similar to Ca (figure not shown) from the infiltrating fluids on the Meridiani rocks. These results further suggest that the  $\text{Fe}^{2+}$  might have later oxidized to  $\text{Fe}^{3+}$  at Meridiani. Furthermore, application of the “geochemical divide” principle [9,10] to the results obtained here suggests that the  $\text{Fe}^{2+}/\text{SO}_4 > 1$  in these fluids before the onset of progressive evaporation.

**References:** [1] Rao M. N. et al. (2005) *JGR*, 110, E12S06, doi: 10.1029/2005JE002470. [2] Rao M.N.et.al.(2008)*JGR*,113, doi: 10.1029/2007JE002958. [3] Clark B. C. et al. (2005) *Earth Planet. Sci. Lett.*, 240, 73-94. [4] McLennan S. M. et al., (2005) *Earth Planet. Sci. Lett.*, 240, 95-121. [5] Gellert R. et al. (2006) *JGR*, 111, doi: 10.1029/2006JE002555. [6] Reider R. et al. (2004) *Science*, 306, 1746-17949. [7] Langmuir C. H. et al. (1978) *Earth Planet. Sci. Lett.*, 37, 380-392. [8] Faure G. (1998) *Principles and Applications of Geochemistry*, Prentice-Hall, 600pp. [11]. [9] Hardie L. A. and Eugster H.P. (1970) *Mineral. Soc. Am. Spec. paper*, 3, 273-290. [10] Eugster H. P. and Jones B. F. (1979) *Am. J. Sci.* 279, 609-631.

#### Figures and Captions :

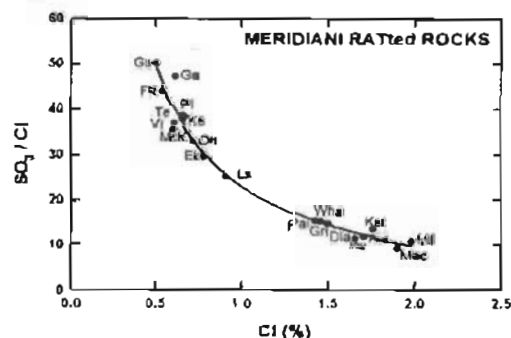


Fig. 1.  $\text{SO}_3/\text{Cl}$  vs Cl on abraded rocks (RAT) from Meridiani (Endurance, Eagle and Fram craters).

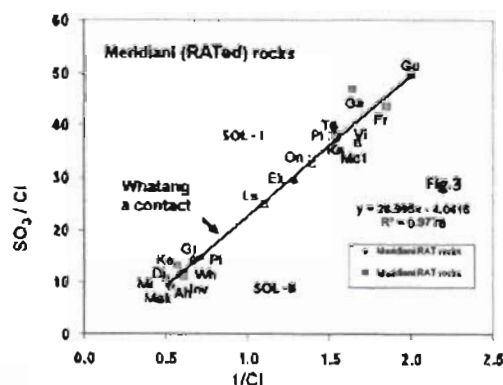


Fig.2.  $\text{SO}_3/\text{Cl}$  vs  $1/\text{Cl}$  plot for Meridiani (RAT) rocks

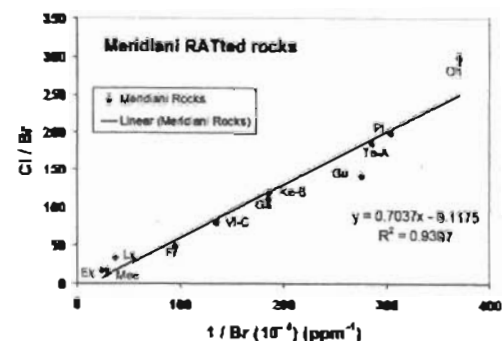


Fig.3.  $\text{Cl}/\text{Br}$  vs  $1/\text{Br}$  plot for Meridiani (RAT) rocks

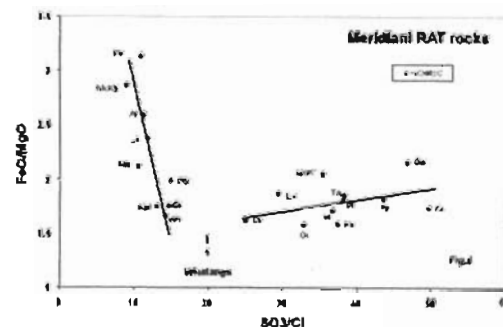


Fig.4.  $\text{FeO}/\text{MgO}$  vs  $\text{SO}_3/\text{Cl}$  plot for Meridiani (RAT) rocks